

Exact exchange-correlation potential of a ionic Hubbard model with a free surface.

V. Brosco, Z.-J. Ying, J. Lorenzana

ISC-CNR and Dipartimento di Fisica, University of Rome “La Sapienza”, P.le A. Moro 2, I-00185 Rome, Italy

(Dated: August 22, 2012)

We use Lanczos exact diagonalization to compute the exact exchange correlation potential (v_{xc}) of a Hubbard chain with large binding energy (“the bulk”) followed by a chain with zero binding energy (“the vacuum”). Several results of density functional theory in the continuum (sometimes controversial) are verified in the lattice. In particular we show explicitly that the fundamental gap is given by the gap in the Kohn-Sham spectrum plus Δ_{xc} , the jump on v_{xc} in the bulk when a particle is added. The presence of a staggered potential and a nearest-neighbor interaction V allows to simulate a ionic solid. We show that in the small hopping amplitude limit $\Delta_{xc} = V$ in the ionic regime, while in the Mott regime Δ_{xc} is determined by the Hubbard U interaction. In addition we show that correlations generates a new potential barrier in v_{xc} at the surface.

Density functional theory[1–3] (DFT) plays a major role in our understanding of ground state properties of materials. However most approximate DFT approaches fail to predict the fundamental gap Δ_C of insulators and semiconductors (band gap problem) [4–13], in systems ranging from bulk Silicon [8] to ZnO [12] and other correlated insulators[13].

At the heart of almost all practical computational schemes based on density functional theory [1–3] (DFT) lies the assumption, first introduced by Kohn and Sham[2], that the ground-state density ρ of an interacting electron gas in an external potential can be reproduced by a system of non-interacting electrons in an effective potential v_{KS} . The effective potential can be expressed as the sum of three contributions: the external potential, v , the Hartree potential v_H , and a term which accounts for exchange and correlation effects, v_{xc} . The latter is the functional derivative of a universal “divine functional”[14] of the density whose precise form is not known. As first discussed by Perdew *et al.* [4, 5] and by Sham and Schüller [6], the exchange-correlation potential v_{xc} may have a jump of order one when one particle is added to a solid. This jump, which is absent in local and semi-local approximate functionals,[9, 12] may account for the error on the fundamental gap according to [5, 6]

$$\Delta_C = \Delta_{KS} + \Delta_{xc}. \quad (1)$$

where Δ_{KS} denotes the single-particle gap in the Kohn-Sham non-interacting system. The size of this effect has been however long debated [7–11, 15–17].

In a pioneering work Gunnarsson and Schönhammer[7] studied a model of a one dimensional spinless insulator and found that Δ_{xc} is small in the band insulating regime. Other authors have, however, argued that the discontinuity should be large and it should account for a large part of the band gap problem[8, 10, 15]. The elusiveness of Δ_{xc} is such that even its existence has been recently questioned[16].

Eq. (1) is based on the DFT version of Koopmans theorem[4, 18] which identifies the ionization energy with

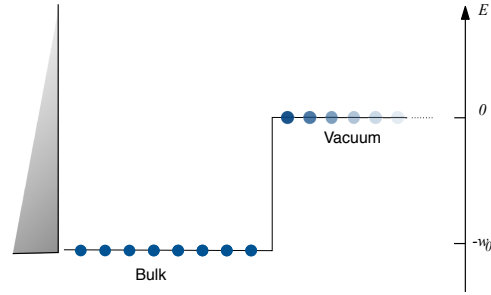


FIG. 1: Structure of the system consisting of L_B bulk and L_V vacuum sites. The bulk sites have a large binding energy, w_0 .

the highest occupied Kohn-Sham eigenvalue and whose validity has also been subject of controversies[4, 18–22]. This debate along with the need to understand and correct the deficiencies of approximate DFT approaches has recently revived the interest in small systems (zero dimensional) whose exchange-correlation potential can be calculated exactly or very accurately[23–26] or lattice systems where DFT or approximate lattice DFT schemes can be tested and analyzed in a controlled environment retaining many of the subtleties of the many-body problem in extended systems which can not be accessed otherwise[27–35].

In this work we use lattice DFT to investigate the band-gap problem. We calculate numerically the exact exchange-correlation potential of a correlated insulator described by a generalized Hubbard model which can be tuned continuously from a ionic to a Mott insulating regime[36]. We consider an open system with a free surface which removes any possible ambiguity related to the validity of Koopmans theorem and or Eq. 1. *i.e.* we compute each term on the left and right of Eq. 1 separately which serves as a numerical test of the equation itself. We find that the contribution of the exchange-correlation potential discontinuity to the charge gap is non-negligible in both regimes. The presence of the surface also allows us to highlight the appearance of an anomaly in the exact

exchange correlation potential in the vacuum sites which appears as the system enters the Mott phase.

We consider a Hubbard chain of L_B sites with a large binding energy called “the bulk” followed by a chain of L_V sites with zero binding energy termed “the vacuum” with open boundary conditions as shown in Fig. 1. The bulk is thus a truly open system which is crucial to completely determine the exchange-correlation potential.

The total Hamiltonian can be written as $H = T + H_U + H_v$ with

$$\begin{aligned} T &= -t \sum_{x\sigma} (c_{x\sigma}^\dagger c_{x+1\sigma} - n_{x\sigma} + H.c.) \\ H_U &= U \sum_x n_{x\uparrow} n_{x\downarrow} + V \sum_{x\sigma} n_{x\sigma} n_{x+1\sigma} \\ H_v &= \sum_{x\sigma} v_x n_{x\sigma}, \end{aligned} \quad (2)$$

where $c_{x\sigma}^\dagger$ creates an electron with spin $\sigma = \uparrow, \downarrow$ at site x , U and V are respectively the Hubbard interaction and nearest-neighbor interaction, t is the nearest-neighbor hopping and we set $n_{x\sigma} = c_{x\sigma}^\dagger c_{x\sigma}$. We included a constant energy shift in the lattice kinetic energy T so that single particle energies are measured from the bottom of the band. In order to simulate the work function of a solid the potential in the bulk is taken as $v_x = -w_0 + \delta(-1)^x$ where w_0 is a large positive constant such that all particles in the system are bound in the bulk region and the second term is a site dependent potential. The potential in the vacuum is by definition $v_x = 0$.

We apply DFT to this problem by considering the site occupancy $\rho_x = \sum_\sigma \langle n_{x\sigma} \rangle$ as the fundamental variable[7]. The charge density and the ground state energy are obtained using Lanczos exact diagonalization[37]. The exchange correlation potential is obtained from the exact density inverting the Kohn-Sham problem[38].

In order to illustrate our capability obtain the absolute value of the exchange correlation potential we first consider the case of a constant external potential in the bulk ($\delta = 0$) and vanishing nearest-neighbor interaction $V = 0$. This corresponds to the case of a uniform Hubbard model which has been discussed in Refs. [7, 27].

In the upper and lower panels of Fig. 2 we plot respectively the electron density and the exact effective potential for $U = 6$ and $w_0 = 8$. We consider in particular the case when the bulk is half-filled, *i.e.* $N = L_B$, and the cases of a bulk above and below half-filling, $N = L_B \pm 1$.

As shown in the lower panel, while the change in the potential on the bulk on going from $N = L_B - 1$ case to the $N = L_B$ is small and can be attributed to a $O(1/N)$ effect, there is a sizable $[O(1)]$ jump on going from $N = L_B$ to $N = L_B + 1$. For all other fillings different from $N = L_B$ we find that the one particle addition jump is $[O(1/N)]$.

The jump for $N = L_B$ determines Δ_{xc} which we define

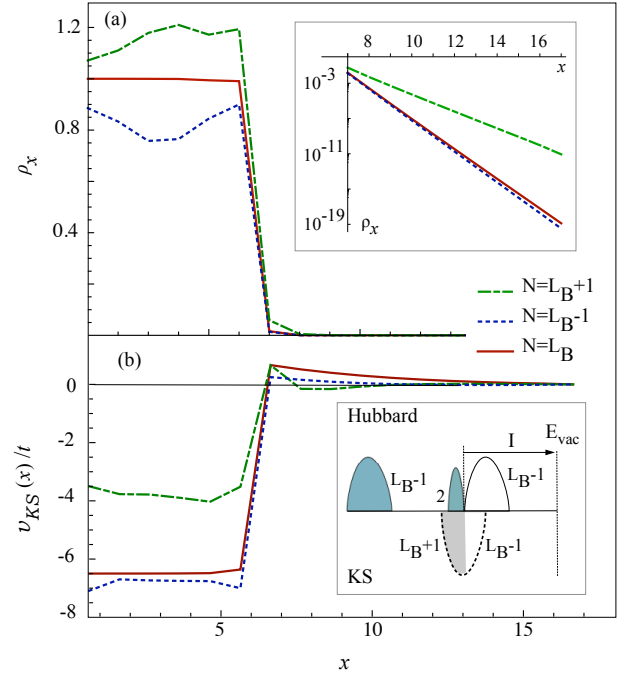


FIG. 2: Panel (a) and (b) show respectively the charge density and the KS potential for $U = 6$ at three different fillings, namely $N = L_B$, $N = L_B \pm 1$. The inset of panel (a) presents a logarithmic plot of the density in the vacuum while the inset of panel (b) presents a schematic comparison between the spectrum of the Hubbard model and of the effective KS system for $N = L_B + 1$. Other parameters: $w_0 = 8t$, $v_x = 0$, $L_B = 6$ and $L_V = 11$.

as

$$\Delta_{xc} = \sum_x |\varphi_{N+1}^{N+1}(x)|^2 (v_{KS}^{N+1}(x) - v_{KS}^N(x)) \quad (3)$$

with v_{KS}^N the N -particle Kohn-Sham potential and $\varphi_{\nu}^N(x)$, ϵ_{ν}^N the corresponding ν -th eigenvector and eigenvalue respectively. Notice that the shift of the potential is not perfectly constant in all the bulk region due to finite size effects. Assuming that $\varphi_{N+1}^{N+1}(x)$ is bound in the bulk region Eq. (3) correctly converges to the expected constant shift of the bulk in the thermodynamic limit. For finite systems we show below that with the present definition Eq. (1) is satisfied with surprisingly small finite size corrections. Similar results are obtained if the slightly different definition of Ref. [6] is used[39].

Fig. 3 shows the U dependence of the exact charge gap of the $N = L_B$ electron system defined as $\Delta_C \equiv I^N - A^N$ where I^N and A^N indicate respectively the ionization energy and the electron affinity of the N -particle system, $I^N \equiv E_0^{N-1} - E_0^N$, $A^N \equiv E_0^N - E_0^{N+1}$ with E_0^N denoting the ground state energy of the N -particle system obtained with the same Lanczos computation. We also show $\Delta_{xc} + \Delta_{KS}$ where Δ_{KS} is the exact KS gap, *i.e.* the gap in the spectrum of the effective non-interacting

N -particle Kohn-Sham system. We see that indeed Eq. 1 is well fulfilled. As discussed below the Kohn-Sham gap should vanish in the thermodynamic limit for a Hubbard chain so its finiteness is a finite size effect.

The charge density in the vacuum remains for all fillings much smaller than 1 and decays exponentially as shown by the logarithmic plot in the inset of Fig. 2 (upper panel). The change in the density decay rate in the vacuum as the filling becomes larger than one ($N > L_B$), reflects a change in the ionization energy due to electronic correlations. Indeed as explained e.g. by Almbladh and von Barth[18, 38] the density decay rate, κ , is related to the ionization energy. In particular in the lattice one can show that [38] $\kappa = 2 \cosh^{-1}(I^N/2t)$. An accurate computation of the density profile in the vacuum region is what allow us to compute the absolute value of the Kohn-Sham potential in the bulk. More precisely the potential in the bulk is referred to the vacuum site furthest to the interface which is assumed to have zero Kohn-Sham potential.

The inset of Fig. 3 shows schematically the behavior of the Kohn-Sham bands in a large Hubbard chain which can be solved exactly with periodic boundary conditions[40]. The charge is uniform and thus the Kohn-Sham potential is a constant[41] which, without the vacuum, remains undetermined. However we know that the chemical potential as a function of filling has a jump at half-filling equal to the Mott-Hubbard gap Δ_{Mott} . If we loosely consider the atoms of the Hubbard chain to have a large constant binding energy $v_x = -w_0$ and to be immersed in a “vacuum” with zero binding energy we expect that the ionization energy will have a jump at half-filling due to the jump in the chemical potential. Due to DFT Koopman’s theorem the center of the bands and Kohn-Sham potential will have a jump at half-filling such that $\Delta_{xc} = \Delta_{Mott}$ as shown schematically in the inset of Fig. 3. In Fig. 3 we also see that in spite of the bulk chain being short ($L_B = 6$), Δ_{xc} approximately coincides with Δ_{Mott} for the infinite system calculated by Bethe Ansatz showing that this picture[7, 27] is indeed correct and finite size corrections to Δ_{xc} are negligible.

In Figure 2 we also note the appearance of a peak at the boundary between vacuum and bulk, on the vacuum side with width and height depend on the filling. Just as the leading (smallest) decay rate of the wave function is determined by the first ionization energy, ionization from deeper states will determine subleading decays rates which are important at short distances[18]. Thus to better understand the origin of this peak it is useful to compare the photoemission spectrum of the Hubbard model and the Kohn-Sham spectrum. At large U and for $N = L_B + 1$ particles the removal spectra of both systems is very different as shown schematically in the inset of Fig. 2. In the Hubbard model only two states are available at low energy[42] while in the Kohn-Sham spectrum we have $L_B + 1$ states available. This large

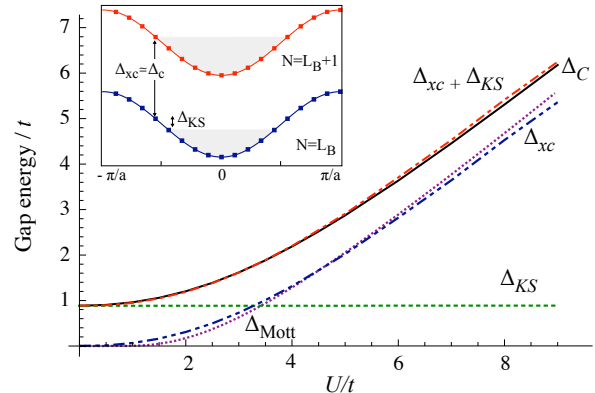


FIG. 3: Exact charge gap Δ_C , Kohn-Sham gap, Δ_{KS} and contribution of the xc -potential jump, Δ_{xc} for a half-filled Hubbard chain with $L_B = 6$ sites. Δ_{Mott} is the Mott gap for an infinite system calculated using Bethe Ansatz[40]. The inset shows Kohn-Sham band structure of a uniform Hubbard chain at half-filling ($N = L_B$) and with one added electron ($N = L_B + 1$).

spectral difference would imply different subleading decay rates, with a tendency of the Kohn-Sham system to have a charge density larger than in the interacting system close to the boundary. This tendency is compensated by the appearance of the peak in the Kohn-Sham potential. Thus the anomalous transfer of spectral weight in the Hubbard model, which is the hallmark of strong electron correlation[42], reflects in the appearance of the barrier.

Now we consider the transition between a Mott insulator and an ionic insulator. In order to simulate a binary compound we consider the case in the presence of δ , the Hubbard U which for simplicity is taken equal on all atoms and a nearest neighbor repulsion V . The system shows a transition from a Mott insulating regime to a Mott insulating regime when $U \sim 2\delta + zV$ with $z = 2$ the coordination number[36]. In the atomic limit one finds that $\Delta_c^{Mott} = U - 2\delta$ in the Mott regime and $\Delta_c^{Ionic} = 2\delta + 2zV - U$ in the ionic regime with both gaps coinciding at the transition. Notice that the latter is larger than the nearest neighbor charge transfer energy corresponding to the excitation of a Frenkel exciton $\Delta_{ex} = \Delta_c^{Ionic} - V$ and which becomes relevant below.

Figure 4 shows again that Eq. (1) is well satisfied with negligibly finite size corrections[38]. (a) and (b) show respectively the results for $V = 0$ and $\delta = 2t$ and for $V = 0.5t$ and $\delta = t$. As one can easily check the total charge gap at $U = 0$ for small t is the same in the two cases. However in the first case we have $\Delta_C \simeq \Delta_{KS}$ in the ionic insulator and $\Delta_C \simeq \Delta_{xc}$ in the Mott-insulating phase, while in the second case we have a finite contri-

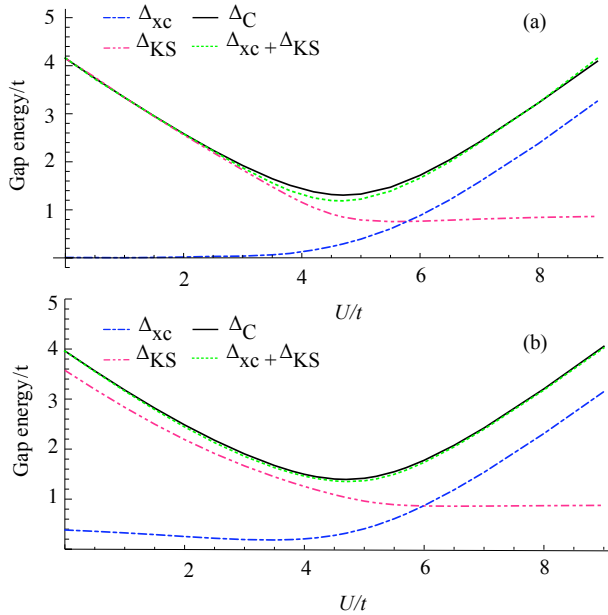


FIG. 4: Panel (a) and (b) show the different contributions to the gap, Δ_{KS} and Δ_{xc} and compare their sum to the exact charge gap calculated by Lanczos diagonalization, Δ_C . The parameters in the two panels are chosen to have the same total charge gap at $U=0$ in the small hopping limit. Parameters are in panel (a) $\delta = 2t$, $V = 0$, in panel (b) $\delta = t$, $V = 0.5t$. In both panels we set $w_0 = -6t + U/2$ and the potential of the site closer to the bulk-vacuum boundary has been chosen to correct boundary effects.

bution of Δ_{xc} to the gap in both regimes. Clearly the appearance of a finite Δ_{xc} in the ionic regime is linked to the presence of the non local interaction V . This can be easily understand by considering the limit of weak tunneling $t \ll \Delta_{ex}$. Using perturbation theory one easily finds that the amount of charge transferred from odd to even sites is $\delta\rho = 4t^2/\Delta_{ex}^2$. For a uniform chain, by symmetry, the difference in the Kohn Sham potential between even and odd sites is equal to the Kohn Sham gap. Applying the same perturbative argument to the Kohn-Sham system we arrive to the conclusion that to match the exact density $\Delta_{KS} = \Delta_{ex}$ therefore $\Delta_{xc} = V$. It is easy to check that these relations are valid in any dimension. They are in good agreement with the numerical results of Fig. 4 in the ionic regime.

In general we expect that in strongly ionic insulators to a good approximation the Kohn-Sham gap matches the first Frenkel exciton and that Δ_{xc} is given by its binding energy respect to the fundamental gap. While in ionic salts the Frenkel exciton is easily accessible experimentally the fundamental gap is difficult to measure and is often obtain by a theoretical fit to the observed optical

spectra[43]. In any case matching of the Frenkel gap by Δ_{KS} puts a strong constraint on density functionals in strong ionic insulators.

To conclude we have computed the exact exchange correlation potential of a correlated extended system including the (usually undetermined) absolute value respect to a vacuum level. This has allowed the first explicit numerical test of Eq. (1) in a model ionic/Mott insulator which dissipates any possible doubt on the validity of this equation or of the underlying DFT-Koopmans theorem. For Mott insulators we have shown that the discontinuity of the exchange correlation potential is given by the Mott Hubbard gap which is of the order U for strong correlation. On the other hand in a strong ionic insulator the discontinuity is determined by the nearest neighbor repulsion V which provides a simple estimate of this elusive quantity. In addition we have shown that a surface correlation barrier appears in the effective potential of a correlated system when the removal spectrum of the system is very different from the removal spectrum of the Kohn-Sham system as is expected to occur in electron doped Mott insulators.

This work was supported by the Italian Institute of Technology through the project NEWDFESCM. V.B. is indebted to L. Chiodo for discussions.

-
- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
 - [2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
 - [3] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
 - [4] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
 - [5] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).
 - [6] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).
 - [7] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **56**, 1968 (1986).
 - [8] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).
 - [9] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008).
 - [10] M. Grüning, A. Marini, and A. Rubio, J. Chem. Phys. **124**, 154108 (2006).
 - [11] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **100**, 146401 (2008).
 - [12] S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).
 - [13] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, in *Quasiparticle Calculations in Solids* (Elsevier, 1999), Vol. 54, pp. 1–218.
 - [14] A. E. Mattsson, Science **298**, 759 (2002).
 - [15] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **60**, 1582 (1988).
 - [16] F. E. Zahariev and Y. A. Wang, Phys. Rev. A **70**, 042503 (2004).
 - [17] E. Sagvolden and J. P. Perdew, Phys. Rev. A **77**, 012517 (2008).

- [18] C. O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).
- [19] V. Russier, Phys. Rev. B **45**, 8894 (1992).
- [20] L. Kleinman, Phys. Rev. B **56**, 12042 (1997).
- [21] J. P. Perdew and M. Levy, Phys. Rev. B **56**, 16021 (1997).
- [22] I. Dabo *et al.*, Phys. Rev. B **82**, 115121 (2010).
- [23] I. D’Amico and G. Vignale, Phys. Rev. B **59**, 7876 (1999).
- [24] E. J. Baerends, Phys. Rev. Lett. **87**, 133004 (2001).
- [25] P. Gori-Giorgi and A. Savin, Int. J. Quantum Chem. **109**, 2410 (2009).
- [26] A. Makmal, S. Kümmel, and L. Kronik, Phys. Rev. A **83**, 062512 (2011).
- [27] N. A. Lima, L. N. Oliveira, and K. Capelle, Europhys. Lett. **601** (2007).
- [28] N. A. Lima, M. F. Silva, L. N. Oliveira, and K. Capelle, Phys. Rev. Lett. **90**, 146402 (2003).
- [29] J. P. Bergfield, Z. F. Liu, K. Burke, and C. A. Stafford, Phys. Rev. Lett. **108**, 066801 (2012).
- [30] E. M. Stoudenmire, L. O. Wagner, S. R. White, and K. Burke, arXiv:1107.2394.
- [31] S. Kurth *et al.*, Phys. Rev. Lett. **104**, 236801 (2010).
- [32] G. Stefanucci and S. Kurth, Phys. Rev. Lett. **107**, 216401 (2011).
- [33] F. Evers and P. Schmitteckert, arXiv:1106.3658.
- [34] P. Tröster, P. Schmitteckert, and F. Evers, Phys. Rev. B **85**, 115409 (2012).
- [35] D. Karlsson, A. Privitera, and C. Verdozzi, Phys. Rev. Lett. **106**, 116401 (2011).
- [36] N. Nagaosa and T. Jun-ichi, J. Phys. Soc. Japan **55**, 2735 (1986).
- [37] B. Bauer *et al.*, J. Stat. Mech. **2011**, P05001 (2011).
- [38] See Supplemental Material at [URL will be inserted by publisher] for detail on the numerical methods, an analysis of finite size effects and a generalization of Koopmans theorem for the lattice.
- [39] Other authors define Δ_{xc} from Eq. (1) which makes it trivially fulfilled. The present definition, instead, preserves the full physical significance of the equation.
- [40] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).
- [41] Notice that the Mott insulator is described by a metallic band in Khon-Sham despite the description being formally exact. Δ_{KS} is of order $1/L_B$ (*c.f.* inset of Fig. 3) thus $\Delta_c = \Delta_{xc}$ in the thermodynamic limit.
- [42] H. Eskes, M. B. J. Meinders, and G. A. Sawatzky, Phys. Rev. Lett. **67**, 1035 (1991).
- [43] M. Rohlfing and S. G. Louie, Phys. Rev. B **62**, 4927 (2000).

Supplementary material to “Exact exchange-correlation potential of a Ionic/Mott insulator with a free surface.”

Valentina Brosco, Z.-J. Ying, J. Lorenzana

ISC-CNR and Dipartimento di Fisica, University of Rome “La Sapienza”, P.le A. Moro 2, I-00185 Rome, Italy

Exact Exchange correlation potential and proof of Koopmans theorem in the lattice

To calculate the exact Kohn-Sham (KS) potential, *i.e.* the effective non-interacting potential which corresponds to the exact density, we adopt the following strategy: we first obtain the ground-state density by applying Lanczos diagonalization⁴ to the “bulk+vacuum” chain, we then extract the KS potential by minimizing the difference between the KS density and the exact one for all values of the KS potential.

The KS density is as usual expressed in terms of KS orbitals, $\varphi_i(x, \sigma)$, as

$$\rho_{KS}(x) = \sum_{i,\sigma} |\varphi_i(x, \sigma)|^2.$$

The orbitals $\varphi_i(x, \sigma)$ are in turn defined through the well-known KS equations,

$$(\hat{T}_s + v_{KS}[x; \rho])\varphi_i(x, \sigma) = \varepsilon_i \varphi_i(x, \sigma) \quad (1)$$

where \hat{T}_s is defined by $\hat{T}_s \varphi_i(x, \sigma) \equiv -t(\varphi_i(x+1, \sigma) + \varphi_i(x-1, \sigma) - 2\varphi_i(x, \sigma))$, $v_{KS}[x; \rho]$ is the effective KS potential and ε_i are the KS energies. To find the exact KS potential, we thus simply minimize relative mean square error on the density *i.e.* we calculate:

$$\min_{v_{KS}(x)} \sum_{x,\sigma} \frac{|\rho(x, \sigma) - \rho_{KS}(x, \sigma)|^2}{|\rho(x, \sigma)|^2} \quad (2)$$

where ρ denotes the exact density obtained by Lanczos diagonalization. After the minimization the relative error on the density is smaller than 10^{-5} *i.e.* $|1 - \rho_{KS}/\rho| \lesssim 10^{-5}$. As we now show, such a high accuracy is necessary to correctly describe the asymptotic decay of the density in the vacuum and to satisfy “Koopmans theorem” of DFT. This theorem, which identifies the highest occupied KS eigenvalue with the exact ionization energy, has been discussed and proved by several authors for standard DFT in the “continuum”, here we extend the proof to lattice systems

To prove “Koopmans theorem” in the lattice we follow the route underlined by Almbladh and von Barth³ and we introduce the quasiparticle amplitudes, $f_s(x) = \langle N-1, s | c_{x\sigma} | N, 0 \rangle$, where $|N, 0\rangle$ and $|N, s\rangle$ denote respectively the ground and the s -th excited state of the full N -electron Hamiltonian.

Considering that in the vacuum sites the density is very small and decays exponentially with the distance from the surface for our parameter choice then, following the

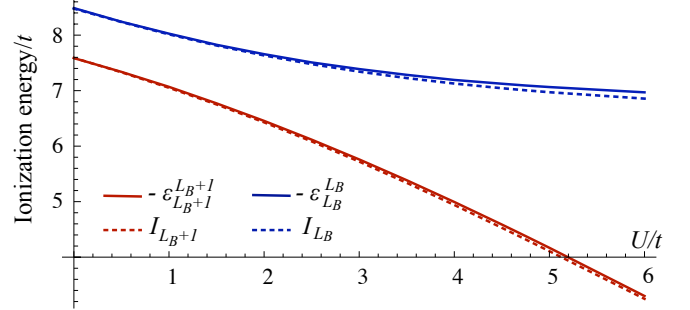


FIG. 1: Ionization energy computed from the exact ground state energies compared with the highest occupied Kohn-Sham eigenvalue for the system with L_B and $L_B + 1$ particles as a function of U/t for constant bulk potential $w_0 = -8t$.

same reasoning as in Ref. 3, one can show that many-body effects become asymptotically irrelevant. Therefore, deep in the vacuum, the quasiparticle amplitudes satisfy the Schrödinger like equation

$$-t(f_{x+1,\sigma}^s + f_{x-1,\sigma}^s - 2f_{x,\sigma}^s) - f_{x,\sigma}^s \Delta E_s = 0 \quad (3)$$

where ΔE_s indicates the difference between the ground state energy of the N -particle system and energy s -th excited level of the $N-1$ -particle system, $\Delta E_s = E_0^N - E_s^{N-1}$. Solving this recursive equation we obtain the following result for the decay of the ground-state quasiparticle amplitude, f_0 in the vacuum:

$$f_0(x) \simeq e^{-\beta x} \quad (4)$$

with $\beta = \cosh^{-1}(\frac{I_N}{2t})$, I_N being the ionization energy $I_N = -\Delta E_0$ of the N -particle system. For comparison in the continuum the decay rate is given by $f_0(r) \propto e^{-\kappa r}$ with $\kappa = \sqrt{2m_e I}$ where m_e denotes the electron mass.

Now considering that the density can be expressed in terms of the quasi-particle amplitudes as, $\rho_{x\sigma}^N = \sum_s f_s^*(x\sigma) f_s(x\sigma)$, and that all the quasi-particle amplitudes with $s > 0$ decay exponentially faster than f_0 , we can assume that the exponential tail of the density far from the surface of a finite system will be governed by the ground state amplitude f_0 . The information on the ionization energy is therefore encoded in the decay of the density far from the bulk system’s surface and it can be obtained in a DFT calculation. In particular, the relation between the ionization energy and the highest Kohn-Sham eigenvalue becomes clear if we consider the analogy between equation (3) and Kohn-Sham equations, Eqs. (1). We note indeed that, since the effective potential can be chosen to vanish in the vacuum far from the

surface, in Kohn-Sham formalism the decay of the density is simply governed by the highest occupied Kohn-Sham level which thus coincides with the ionization energy.

The ionization energy as a function of U is shown in Fig. 1 : we see that Koopmans theorem of DFT is very well verified, the small error, within 2%, is due to the finite size of the vacuum chain.

Charge gap, Kohn-Sham gap and exchange correlation potential discontinuity

For sake of completeness we recall here the derivation of the relation between the charge-gap and the exchange-correlation potential shift starting from Koopmans theorem, this also will allow us to identify the corrections due to finite size effects.

By applying Koopmans theorem Δ_C can be rewritten as follows:

$$\Delta_C = \Delta_{KS} + \varepsilon_{N+1}^{N+1} - \varepsilon_{N+1}^N \quad (5)$$

where ε_N^M indicates the N -th Kohn-Sham level of the M -particle system and the gap in the Kohn-Sham spectrum of the N -particle system is given by $\Delta_{KS} = \varepsilon_{N+1}^N - \varepsilon_N^N$.

Using Kohn-Sham equations for the system with N and $N+1$ particles the charge gap can be further partitioned as the sum of four terms, namely

$$\Delta_C = \Delta_{KS} + \Delta_{xc} + \Delta_\varphi + \Delta_T \quad (6)$$

where Δ_{xc} is the exchange-correlation gap introduced in the article, essentially equivalent to the one used in the literature (see e.g. Ref.[1])

$$\Delta_{xc} = \sum_x |\varphi_{N+1}^{N+1}(x)|^2 (v_{KS}^{N+1}(x) - v_{KS}^N(x)) \quad (7)$$

while Δ_φ and Δ_T are due to the relaxation of the $N+1$ -th Kohn-Sham orbital induced by the addition of a particle,

$$\Delta_T = \sum_x \left(\varphi_{N+1}^{N+1}(x) \hat{T}_s \varphi_{N+1}^{N+1}(x) - \varphi_{N+1}^N(x) \hat{T}_s \varphi_{N+1}^N(x) \right), \quad (8)$$

$$\Delta_\varphi = \sum_x (|\varphi_{N+1}^{N+1}(x)|^2 - |\varphi_{N+1}^N(x)|^2) v_{KS}^N(x). \quad (9)$$

where $v_{KS}^N(x)$ denotes the effective potential of the N -particle system.

For a translationally invariant system both Δ_φ and Δ_T become of order $1/N$ and can be neglected in the thermodynamic limit. Since the difference $\delta v_{KS}(x) = v_{KS}^{N+1}(x) - v_{KS}^N(x)$ becomes constant, in this limit, equation 6 reduces to the well-know relation between the charge gap and the exchange-correlation potential discontinuity shown e.g. in Ref. [2].

Interestingly we find that Δ_φ and Δ_T tend to cancel in finite systems in all interaction regimes. As an example

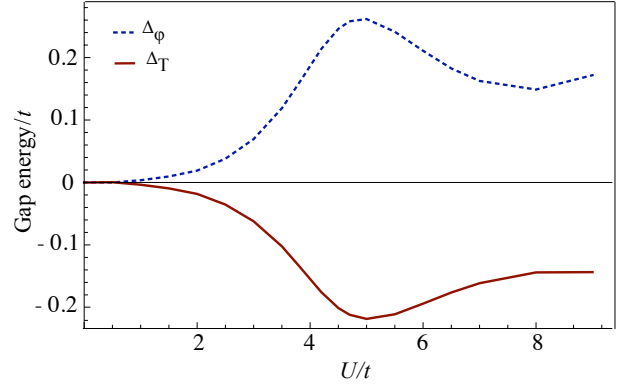


FIG. 2: Corrections to the charge gap, Δ_φ and Δ_T as functions of the ratio, U/t . The bulk potential is $v_x = 2(-1)^x$ while the nearest-neighbor interaction parameter V equals zero. Similar results are obtained both for $V \neq 0$ and for $v_x = 0$.

in Figure 2 we plot the two contributions as a function of U/t for the ionic Hubbard model with $v_x = 2(-1)^x$ and $V = 0$, as one can see the two terms are finite but with opposite signs.

By applying perturbation theory it is not difficult to show that the cancellation stems directly from the definition of exchange-correlation gap given in Eq. (7). The effective potential, v_{KS}^{N+1} , of the $N+1$ particle system can be indeed related to the potential, v_{KS}^N , as follows

$$v_{KS}^{N+1} = v_{KS}^N + C + \Delta v \quad (10)$$

where C is a constant shift, $C = 1/(L_B + L_V) \sum_x (v_{KS}^{N+1} - v_{KS}^N)$, which accounts for the discontinuity and remains finite in the infinite size limit and Δv is a weak site dependent modulation such that $\sum_x \Delta v = 0$ which vanishes in the infinite size limit. Starting from Eq. (10), by applying perturbation theory in Δv we obtain the following expression for $\varepsilon_{N+1}^{N+1} - \varepsilon_{N+1}^N$:

$$\begin{aligned} \varepsilon_{N+1}^{N+1} - \varepsilon_{N+1}^N &\simeq C + \langle \varphi_{N+1}^N(x) | \Delta v | \varphi_{N+1}^N \rangle + \\ &+ \sum_{\nu \neq N+1} \frac{|\langle \varphi_{N+1}^N | \Delta v | \varphi_\nu^N \rangle|^2}{\varepsilon_{N+1}^N - \varepsilon_\nu^N} \end{aligned} \quad (11)$$

Similarly, by inserting Eq. (10) in Eq. (7) we can recast Δ_{xc} as

$$\Delta_{xc} = C + \langle \varphi_{N+1}^{N+1} | \Delta v | \varphi_{N+1}^{N+1} \rangle \quad (12)$$

Eventually, considering that $\Delta_\varphi + \Delta_T = \varepsilon_{N+1}^{N+1} - \varepsilon_{N+1}^N - \Delta_{xc}$ and expanding the wave-function $|\varphi_{N+1}^{N+1}\rangle$ in Eq. (12) we arrive at the following result:

$$\Delta_\varphi + \Delta_T \simeq - \sum_{\nu \neq N+1} \frac{|\langle \varphi_{N+1}^N | \Delta v | \varphi_\nu^N \rangle|^2}{\varepsilon_{N+1}^N - \varepsilon_\nu^N} \quad (13)$$

From this equation we see that the sum $\Delta_\varphi + \Delta_T$ is of second order in Δv , since the change in the wave-function is of first order in Δv .

With a similar reasoning one can prove that with the definition of Δ_{xc} given in Ref. [1] the finite-size errors to

second order in Δv have the same modulus but opposite sign.

This work was supported by the Italian Institute of Technology through the project NEWDFESCM. V.B. is indebted to L. Chiodo for discussions.

¹ Sham, L. J. & Schlüter, M. Density-Functional Theory of the Energy Gap. Phys. Rev. Lett. **51**, 1888-1891 (1983).

² Perdew, J. P. & Levy, M. Physical Content of the Exact Kohn-Sham Orbital Energies: Band Gaps and Derivative Discontinuities Phys. Rev. Lett. **51**, 1884-1887 (1983).

³ Almbladh, C. O. & von Barth, U. Exact results for the charge and spin densities, exchange-correlation potentials,

and density-functional eigenvalues. Phys. Rev. B **31**, 3231 (1985).

⁴ Bauer, B. et al. (ALPS collaboration) The ALPS project release 2.0: open source software for strongly correlated systems. J. Stat. Mech. P05001 (2011).